

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
19 April 2001 (19.04.2001)

PCT

(10) International Publication Number
WO 01/27050 A1(51) International Patent Classification⁷: C03C 17/36

(21) International Application Number: PCT/EP00/10278

(22) International Filing Date: 13 October 2000 (13.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
99203357.1 14 October 1999 (14.10.1999) EP(71) Applicant (for all designated States except US):
GLAVERBEL [BE/BE]; Chaussée de la Hulpe 166,
B-1170 Brussels (Watermael-Boitsfort) (BE).

(72) Inventor; and

(75) Inventor/Applicant (for US only): DEPAUW,
Jean-Michel [BE/BE]; Glaverbel, Centre R. & D.,
Rue de l'Aurore 2, B-6040 Jumet (BE).

(74) Agents: FARMER, Guy et al.; Glaverbel, Dept. Intellectual Property, Centre R. & D., Rue de l'Aurore 2, B-6040 Jumet (BE).

(81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

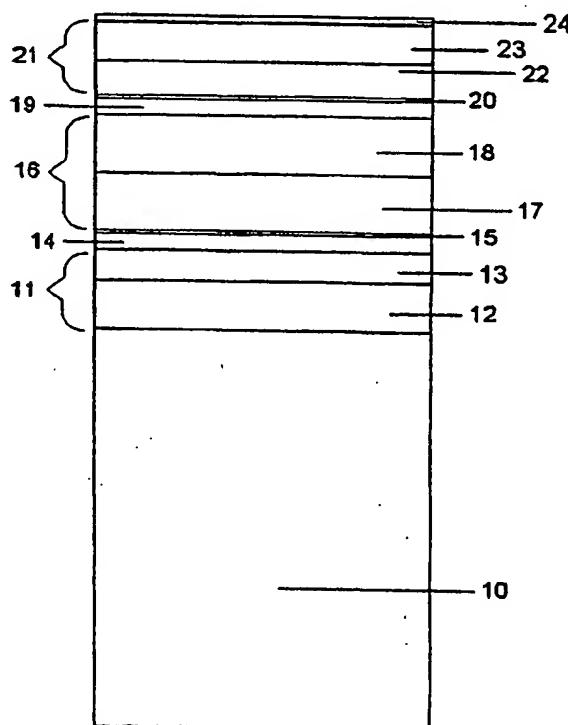
(84) Designated States (regional): Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: GLAZING



(57) Abstract: A glazing panel comprises in sequence at least: a glass substrate, a base antireflective layer comprising at least a base antireflective lower layer and a base antireflective upper layer which is of a different composition to that of the base antireflective lower layer, the base antireflective upper layer comprising a mixed oxide of Zn and at least one additional material X, in which the ratio X/Zn in the base antireflective upper layer is between 0.02 and 0.5 by weight and in which X is one or more of the materials selected from the group comprising Sn, Al, Ga, In, Zr, Sb, Bi, Mg, Nb, Ta and Ti, a first infra-red reflecting layer, a first barrier layer, a central antireflective layer comprising at least a central antireflective lower layer and a central antireflective upper layer which is of a different composition to that of the central antireflective lower layer, the central antireflective lower layer being in direct contact with the first barrier layer and the central antireflective upper layer comprising a mixed oxide of Zn and at least one additional material Y, in which the ratio Y/Zn in the base antireflective upper layer is between 0.02 and 0.5 by weight and in which Y is one or more of the materials selected from the group comprising Sn, Al, Ga, In, Zr, Sb, Bi, Mg, Nb, Ta and Ti, a second infra-red reflecting layer, a second barrier layer, a top antireflective layer. The coating stack of such a glazing panel may provide particularly advantageous levels of the thermal stability so as to facilitate heat treatment of the glazing panel.

Glazing

This invention relates to glazing panels and particularly to glazing panels which are intended to undergo heat treatment following application of a solar control filter.

EP 233003A describes a glazing panel carrying a sputter coated optical filter having the structure: glass substrate/ SnO₂ base dielectric/ first metallic barrier of Al, Ti, Zn, Zr or Ta / Ag / second metallic barrier of Al, Ti, Zn, Zr or Ta / SnO₂ top dielectric. The optical filter is designed to block a significant portion of the incident radiation in the infra red portion of the spectrum whilst allowing passage of a significant portion of the incident radiation in the visible portion of the spectrum. In this way, the filter acts to reduce the heating effect of incident sunlight whilst allowing good visibility through the glazing and is particularly suitable for car windscreens.

In this type of structure, the Ag layer acts to reflect incident infra red radiation; in order to fulfil this role must be maintained as silver metal rather than silver oxide and must not be significantly contaminated by adjacent layers. The dielectric layers which sandwich the Ag layer serve to reduce the reflection of the visible portion of the spectrum which the Ag layer would otherwise provoke. The second barrier serves to prevent oxidation of the Ag layer during sputtering of the overlying SnO₂ dielectric layer in an oxidising atmosphere; this barrier is at least partially oxidised during this process. The main role of the first barrier is to prevent oxidation of the silver layer during heat treatment of the coating (e.g. during bending and/or tempering) of the glazing panel by being oxidised itself rather than allowing passage of oxygen to the Ag layer. This oxidation of the barrier during heat treatment provokes an increase in TL of the glazing panel.

EP 792847A discloses a heat treatable solar control glazing panel which is based on the same principle and has the structure: glass substrate/ ZnO dielectric/ Zn barrier/ Ag / Zn barrier/ ZnO dielectric/ Zn barrier/ Ag / Zn barrier/ ZnO dielectric. The Zn barriers positioned below each of the Ag layers are intended to be oxidised completely during heat treatment and serve to protect the Ag layers from oxidation. As well known in the art, the structure of having two, spaced Ag layers rather than a single Ag layer increases the selectivity of the filter.

EP 275474 A discloses a heat treatable solar control panel having the structure: glass substrate/ zinc stannate dielectric/ Ti barrier/ Ag/ Ti barrier/ zinc stannate dielectric. Ti barriers are generally favoured in this type of heat treatable structure due to their high affinity for oxygen and relative ease with which they can be oxidised to form titanium oxide.

According to one aspect, the present invention provides a glazing panel as defined in Claim 1.

5 The coating layers are preferably deposited by sputtering, preferably magnetron sputtering but other deposition techniques may be used. Different layers of the coating stack may be deposited using different techniques.

The upper layers in the base and central antireflective layers may have the same or substantially the same composition. This may facilitate the use of substantially similar targets to deposit these layers and/or substantially similar deposition conditions.

10 The combination of the defined upper layers in the base and central antireflective layers as part of the defined coating stack may facilitate the production of glazing panels (and particularly of laminated windscreens) having TL greater than 75% once subjected to heat treatment whilst still providing an advantageous combination of repeatable thermal stability during heat treatment, low haze, 15 mechanical and chemical resistance and desired colour in reflection and/or transmission.

One or preferably both of the additional materials X and Y is preferably Sn and/or Al. This may give a particularly advantageous combination of properties.

20 The proportion of Zn in the mixed oxide that forms the base antireflective upper layer and/or that which forms the central antireflective upper layer may be such that ratio X/Zn and/or the ratio Y/Zn is between about 0.03 and 0.3 by weight.

25 Arranging one or each of the upper layers of the base and/or central antireflective layers in direct contact with its overlying infra-red reflecting layer may also facilitate achieving high levels of TL during heat treatment. Alternatively, an addition layer, for example, a barrier layer, may be interposed between one or each of the upper layers of the base and central antireflective layers and its overlying infrared reflecting layer. Such an additional barrier may be a layer comprising Ti and/or 30 comprising an oxide of Ti. The additional barrier layer may have a geometrical thickness of between about 5 Å and 60 Å.

35 The base antireflective upper layer and/or the central antireflective upper layer may have a geometrical thickness of less than about 200 Å, less than about 150 Å, less than about 130 Å or less than about 110 Å. This may provide advantageous mechanical properties to the coating stack, particularly with respect to resistance to peel tests.

The base antireflective upper layer and/or the central antireflective upper layer may have a geometrical thickness of greater than about 30 Å, greater

than about 50 Å greater than about 100 Å. This may provide a sufficient thickness to enhance the properties of the coating stack, particularly with respect to TL obtainable after heat treatment.

The central antireflective lower layer may comprises at least one layer

5 which provides a sufficient block to the migration of oxygen and/or sodium and/or other materials to prevent significant contamination of and/or diffusion of the layers of the coating stack. Preferably, the central antireflective lower layer is in direct contact with the first barrier layer and comprises a material which resists diffusion of the first barrier layer during heat treatment. The combination of a central

10 antireflective lower layer as defined in claim 5 with a first barrier which is deposited at least partially in metallic or substantially metallic form and subsequently oxidised during heat treatment (and particularly a barrier that comprises or consists essentially of metallic Ti when deposited) may permit particularly high thermal stability of the coating stack during heat treatment. It is believed that diffusion of material from the

15 first barrier layer into the central antireflective lower layer during heat treatment and particularly during severe heat treatment may, in some coating stack arrangements be a critical factor in determining thermal stability of the coating stack; the composition of central antireflective lower layer defined in claim 5 may significantly mitigate against such diffusion.

20 The base antireflective lower layer may comprise at least one layer which provides a sufficient block to the migration of oxygen and/or sodium and/or other materials to prevent significant contamination of and/or diffusion of the layers of the coating stack. The use of a base antireflective lower layer as defined in claim 6 may be used to facilitate this whilst, in addition, facilitating the arrangement and control of the deposition conditions.

The use of a top antireflective layer as defined in claim 9 may facilitate the arrangement and control of the deposition conditions for the overall coating stack. In addition, this layer may be arranged to provide a block to migration of oxygen during heat treatment and/or diffusion of the second barrier layer.

25 The top antireflective layer may comprise at least one layer which comprises a mixed oxide of Zn and at least one additional material W, in which the ratio W/Zn in that layer is between 0.02 and 0.5 by weight and in which W is one or more of the materials selected from the group comprising Sn, Al, Ga, In, Zr, Sb, Bi, Mg, Nb, Ta and Ti. This may improve the thermal stability of the coating stack during heat treatment and/or its mechanical or chemical resistance, particularly when used as defined in claim 10.

30 According to further aspects, the invention provides a glazing panel as defined in claim 13 and for use of a glazing panel as defined in claim 14.

According to another aspect, the invention provides a method as defined in claim 15.

The invention may provide an advantageous combination of properties for the glazing, for example:

- 5 • particularly good levels of TL following heat treatment
- particularly good thermal stability during heating of the glazing panel, for example during tempering and/or bending. This may facilitate bending of coated glazing panels, particularly to produce complex shapes, without provoking unacceptable variations in colour over the surface of the glazing panel. Colour variations during heat treatment may be caused by lack of thermal stability of the coating stack when subjected to conditions necessary to bend and/or temper the glass substrate. This aspect may be particularly enhanced by the use of a central antireflective lower layer as defined in claim 5 to inhibit significant diffusion of the first barrier layer;
- 10 • ease and controllability of deposition: the antireflective layers according to the present invention may be deposited more easily and with more control than, for example, Al₂O₃ or SiO₂. Whilst Al₂O₃ and SiO₂ show a good degree of thermal stability they are difficult to deposit using common sputtering techniques.
- 15 • good mechanical resistance: the antireflective layers according to the present invention may be used without prejudicing the mechanical resistance of the coating. In particular, they may perform well in pummel tests when the glazing panel is used in a laminated structure.
- 20 • compatibility with Ag: crystallisation of the Ag layer affects its optical properties. A pure ZnO layer adjacent the Ag can lead to excessive crystallisation of the Ag and to problems of haze in the coating, particularly during heat treatment. However, where an antireflective layer does not consist of ZnO there may be insufficient recrystallisation of the Ag layers resulting in a level of infra red reflection and a level of electrical conductivity in the coating which are below the optimum obtainable. The present invention may be used to favour crystallisation to a sufficient degree to provide good infra red reflecting properties whilst avoiding excessive haze. In particular, it may provide a favourable crystallisation compared with an antireflective layer composed of TiO₂ or SnO₂. One possible explanation for this may be that the presence of the additional material X or Y in the zinc oxide structure may reduce the crystal grain growth in the mixed oxide layer, especially perpendicular to the substrate. This may result in a less crystalline, more amorphous structure which reduces diffusion that might otherwise be likely to occur at crystal grain boundaries.
- 25
- 30
- 35

- production cycle time: an oxide layer which is a mixture of Zn and at least one of the specified addition materials may have a higher refractive index than antireflective layers of, for example, ZnO and SnO₂, which are commonly used in similar structures and yet will be quicker to deposit than known antireflective layers having relatively high refractive indexes, for example, TiO₂. Consequently, this may enable the production cycle time to be improved.
- good selectivity: the higher refractive index may, in addition, facilitate an increase in the selectivity of the coating stack.
- low emissivity, notably an emissivity of less than 0.35, preferably less than 0.32 or less than 0.30, particularly after heat treatment
- low electrical resistance, notably a resistance per square of less than 3 ohms per square, preferably less than 2.8, 2.5 or 2.3 ohms per square, particularly after heat treatment

Particularly advantageous properties may be obtained if additional material X or Y consists

- essentially of Sn
- of Sn with one or more additional materials from the specified group of materials, for example, Ti and Al
- essentially of Al
- of Al with one or more additional materials from the specified group of materials.

The present invention may be particularly advantageous in facilitating manufacture of laminated windscreens or other glazings having colour co-ordinates on the CIElab scale of L* = 40 ±2.5 a* = -6±2.5 b* = -2±2.5. Whilst known coating stacks may enable such windscreens to be manufactured, particularly for simple models which do not require severe heating conditions to provide desired configurations once bent, the present invention, by providing a coating stack which is particularly stable during heat treatment of the glazing panel may allow more complex bent forms to be produced, and/or may provide significantly better industrial yield with less rejects and/or may enable the use of less sophisticated bending methods and/or may ensure that such characteristics may be consistently obtained for industrially produced glazings whilst still providing a TL of at least 75%, and indeed a TL which may be of or above 76%.

Similarly, the present invention may facilitate manufacture of laminated windscreens or other glazings in which the variation of colour ΔE* over the surface of the glazing is less than 2, preferably less than 1.5 or 1.2 and more preferably less than 1 where the variation of colour ΔE* is calculated as:

$\Delta E^* = \sqrt{(L^*{}^2 + a^*{}^2 + b^*{}^2)}$ where L*, a* and b* are measured on the CIElab scale.

5 The variation in colour over the surface of a windscreen will depend on the complexity of the windscreen, the heating method and conditions used to bend the glazing panel and the thermal stability of the coating stack to such colour variations. Whilst prior known coating stacks may enable such low levels of colour variation to be achieved particularly for simple windscreens or under certain heating conditions or with certain levels of rejection for non-conformity, the present invention may be used to facilitate industrial manufacture of such windscreens under 10 significantly more advantageous industrial conditions.

The term "heat treatable glazing panel" as used herein means that the glazing panel carrying the coating stack is adapted to undergo a bending and/or thermal tempering and/or thermal hardening operation without the haze of the so treated glazing panel exceeding 0.5, and preferably without the haze exceeding 0.3. 15 The term "substantially haze free heat treated glazing panel" as used herein means a glazing panel which has been bent and/or thermally tempered and/or thermally hardened and has a haze that does not exceed 0.5 and which preferably does not exceed 0.3. The invention may be particularly advantageous in facilitating manufacture in which a coating stack is deposited on a substantially flat or planar 20 glass substrate to produce a glazing panel which may be subsequently heat treated, for example bent or tempered.

The filter stack may comprise one or more barrier layers underlying and/or overlying the infra red reflecting layer, as is known in the art. Barriers of, for example, one or more of the following material may be used: Ti, Zn, Cr, "stainless 25 steel", Zr, Ni, NiCr, ZnTi NiTi and ZnAl. Such barriers may be deposited, for example, as metallic layers or as sub-oxides (i.e. partially oxidised layers). Alternatively, nitrided barrier layers may also be used. The barrier layers in such coating stacks may serve to protect the infra red reflecting layers from unacceptable levels of degradation during the deposition of overlying layers and/or during heat 30 treatment of the coating stack.

One or more of such barrier layers may comprise the same materials as the mixed oxide layer, particularly the adjacent mixed oxide layer. This may facilitate management of targets and control of deposition conditions and in the latter case may provide good adhesion between the layers and thus good mechanical 35 durability of the coating stack.

Heat treatment may provoke an increase in the TL of the glazing panel. Such an increase in TL may be advantageous in ensuring that TL is sufficiently high for the glazing panel to be used in a vehicle windsreen. TL may

increase in absolute terms during heat treatment by , for example, greater than about 2.5%, greater than about 3%, greater than about 5% , greater than about 8% or greater than about 10%.

5 An example of the present invention will now be described with reference to Fig 1 which is a cross-section through a glazing panel prior to a bending and tempering operation (for ease of representation, the relative thicknesses of the glazing panel and coating layers are not shown to scale).

Example 1

10 Fig 1 shows a double Ag layer, heat treatable, coating layer deposited on a substantially flat or planar glass substrate by magnetron sputtering and having the following sequential structure:

	Reference number	Geometrical thickness	ratio of Sn/Zn by weight
Glass substrate	10	2 mm	
Base antireflective layer comprising:			
lower layer of ZnSnO _x	11		
upper layer of ZnSnO _x	12	200 Å	0.7
Ag	13	100 Å	0.17
Ti overlying barrier	14	100 Å	
Central antireflective layer comprising			
central lower layer of ZnSnO _x	16		
upper layer of ZnSnO _x	17	650 Å	0.7
Ag	18	100 Å	0.17
Ti overlying barrier	19	100 Å	
Top antireflective layer comprising:			
lower layer of ZnSnO _x	21		
upper layer of ZnSnO _x	22	80 Å	0.17
protective overcoat of Ti	23	140 Å	0.7
	24	30 Å	

15 in which ZnSnO_x is a mixed oxide containing Zn and Sn deposited in this example by reactively sputtering a target which is an alloy or mixture of Zn and Sn in the presence of oxygen .

20 Alternatively, a mixed oxide layer may be formed by sputtering a target which is a mixture of zinc oxide and an oxide of an additional material , particularly in an argon gas or argon rich oxygen containing atmosphere.

The Ti barriers are deposited by sputtering a Ti target which is in an argon rich oxygen containing atmosphere to deposit a barrier that is not fully oxidised.

5 The oxidation state in each of the base, central and top ZnSnO_x dielectric layers need not necessarily be the same. Similarly, the oxidation state in each of the Ti barriers need not be the same.

10 Each overlying barrier protects its underlying silver layer from oxidation during sputter deposition of its overlying ZnSnO_x oxide layer. Whilst further oxidation of these barriers layers may occur during deposition of their overlying oxide layers a portion of these barriers preferably remains in metallic form or in the form of an oxide that is not fully oxidised to provide a barrier for and during subsequent heat treatment of the glazing panel.

This particular glazing panel is intended for incorporation in a laminated vehicle windscreens and displays the following properties:

15

Property	Prior to heat treatment <small>see Note 1 below</small>	Following heat treatment <small>see Note 2 below</small>
TL(Illuminant A)	63%	76%
TE (System Moon 2)	38%	42%
haze	0.1	0.25
a*	-10 (glass side)	-6 (external)
b*	+10 (glass side)	-3 (external)
RE (System Moon 2)	29% (glass side)	32%(external)

Note 1: Measured for monolithic glazing panel with coating prior to heat treatment

20 Note 2: Measured following heat treatment at 650° C for 10 minutes followed by bending and tempering, and lamination with clear 2mm glass sheet and 0.76mm clear pvb

Heat treatment preferably causes substantially complete oxidation of all of the barrier layers and of the protective overcoat.

25 The colour co-ordinates of the example are particularly suited to car windscreens as they give a neutral or slightly blue or slightly green appearance in reflection when the windscreen is mounted at an angle in the car body. For other applications, for example architectural applications, the colour in reflection may be adjusted as is known in the art by adjusting the thicknesses of the dielectric layers and/or the infra red reflecting layer(s).

Additional layers may be introduced above, below or between the film stacking arrangement if desired without departing from the invention.

5 In addition to the advantageous optical properties that may be obtained, the example provides a coating layer which may be electrically heated, for example, in an electrically heated car windscreen to provide a de-misting and/or defrosting function with the addition of suitably placed electrical connectors.

The TL of the glazing panel may be adjusted to suit the desired application. For example

10 • if the glazing panel is to be used as a windscreen for the European market, TL may be selected to be greater than 75% (as required by European regulations).

15 • if the glazing panel is to be used as a windscreen for the US market, TL may be selected to be greater than 70% (as required by US regulations).

20 • if the glazing panel is to be used as a vehicle front sidelight, TL may be adjusted to be greater than 70% (as required by European regulations).

25 • if the glazing panel is to be used as a vehicle rear sidelight or a rear window for a vehicle, TL may be selected to be between about 30% and 70%.

Such adjustment of TL may be achieved, for example,

• by adapting the thicknesses of the layers of the coating stack, in particular the thicknesses of the dielectric layers and/or the infra-red reflecting layer(s).

• by combining the coating stack with a tinted glass substrate, for example, in order to increase the selectivity.

• by combining the coating stack with a tinted pvb or other laminating layer.

30 One possible method for determining the composition of the coating stack is by using a SIMS technique. This technique is based upon ionic bombardment of the coating stack with analyses, particularly mass analysis, of the material ejected from the coating stack. Such an analysis may be used to provide an indication of the composition and thickness of the layers of a coating stack.

Glossary

Unless otherwise indicated by the context, the terms listed below have the following meanings in this specification:

a*		colour co-ordinate measured on the CIELab scale at normal incidence
Ag	silver	
Al	aluminium	
Al ₂ O ₃	aluminium oxide	
b*		colour co-ordinate measured on the CIELab scale at normal incidence
Bi	bismuth	
Cr	chromium	
Ga	gallium	
emissivity		emissivity of a given surface at a given temperature is defined as the ratio of the energy emitted by the surface to that of a perfect emitter (black body emissivity = 1.0) at the same temperature. For the glazings in question, emissivity is often measured at 25°C on the coated side of a substrate.
haze		the percentage of transmitted light which in passing through the specimen deviates from the incident beam by forward scattering, as measured in accordance with the ASTM Designation D 1003-61 (Reapproved 1988).
In	indium	
infra red reflecting material		a material that has a reflectance higher than the reflectance of sodalime glass in the band of wavelengths between 780 nm and 50 microns
Mg	magnesium	
Na	sodium	
Nb	niobium	
Ni	nickel	
RE	energetic reflection	the solar flux (luminous and non-luminous) reflected from a substrate as a percentage of the incident solar flux
Sb	antimony	
selectivity		the ratio of the luminous transmittance to the solar factor i.e. TL/TE
SiO ₂	silicon oxide	
SnO ₂	tin oxide	
Ta	tantalum	
TE	energetic transmittance	the solar flux (luminous and non-luminous) transmitted through a substrate as a percentage of the incident solar flux
Ti	titanium	
TL	luminous transmittance	the luminous flux transmitted through a substrate as a percentage of the incident luminous flux
Zn	zinc	
ZnO	Zinc oxide	
Zr	Zirconium	

As will be understood by those skilled in the art, the combination of the antireflective layers in the coating stack serves to reduce the total reflection of the coating stack in the visible portion of the spectrum; the composition and thickness of each antireflective layer may be selected accordingly.

Claims

1. A glazing panel comprising in sequence at least:
 - a glass substrate
 - 5 a base antireflective layer comprising at least a base antireflective lower layer and a base antireflective upper layer which is of a different composition to that of the base antireflective lower layer, the base antireflective upper layer comprising a mixed oxide of Zn and at least one additional material X, in which the ratio X/Zn in the base antireflective upper layer is between 0.02 and 0.5 by weight and in which X is one or more of the materials selected from the group comprising Sn, Al, Ga, In, Zr, Sb, Bi, Mg, Nb, Ta and Ti
 - 10 a first infra-red reflecting layer
 - a first barrier layer
 - 15 a central antireflective layer comprising at least a central antireflective lower layer and a central antireflective upper layer which is of a different composition to that of the central antireflective lower layer, the central antireflective lower layer being in direct contact with the first barrier layer and the central antireflective upper layer comprising a mixed oxide of Zn and at least one additional material Y, in which the ratio Y/Zn in the base antireflective upper layer is between 0.02 and 0.5 by weight and in which Y is one or more of the
 - 20 materials selected from the group comprising Sn, Al, Ga, In, Zr, Sb, Bi, Mg, Nb, Ta and Ti
 - a second infra-red reflecting layer
 - 25 a second barrier layer
 - a top antireflective layer.
2. A glazing panel in accordance with Claim 1, in which the base antireflective upper layer is in direct contact with the first infra red reflecting layer.
3. A glazing panel in accordance with Claim 1 or Claim 2, in which the central antireflective upper layer is in direct contact with the second infra red reflecting layer.
4. A glazing panel in accordance with any preceding claim, in which the upper layers of both the base antireflective layer and the central antireflective layer have a geometrical thickness within the range of about 30 Å to 200 Å.

5. A glazing panel in accordance with any preceding claim, in which the central antireflective lower layer comprises a mixed oxide of Zn and at least one additional material W, in which in which the ratio W/Zn in the central antireflective lower layer is between 0.5 and 2 by weight and in which W is one or more of the materials selected from the group comprising Sn, Al, Ga, In, Zr, Sb, Bi, Mg, Nb, Ta and Ti.
10. A glazing panel in accordance with any preceding claim, in which the base antireflective lower layer comprises a mixed oxide of Zn and at least one additional material W, in which in which the ratio W/Zn in the base antireflective lower layer is between 0.5 and 2 by weight and in which W is one or more of the materials selected from the group comprising Sn, Al, Ga, In, Zr, Sb, Bi, Mg, Nb, Ta and Ti.
15. 7. A glazing panel in accordance with any preceding claim, in which the first barrier layer comprises titanium.
8. A glazing panel in accordance with any preceding claim, in which the second barrier layer comprises titanium.
20. 9. A glazing panel in accordance with any preceding claim, in which the top antireflective layer comprises at least one layer which comprises a mixed oxide of Zn and at least one additional material W, in which W is one or more of the materials selected from the group comprising Sn, Al, Ga, In, Zr, Sb, Bi, Mg, Nb, Ta and Ti.
25. 10. A glazing panel in accordance with any preceding claim, in which the top antireflective layer comprises at least one layer which comprises a mixed oxide of Zn and at least one additional material W, in which in which the ratio W/Zn in that layer is between 0.02 and 0.5 by weight and in which W is one or more of the materials selected from the group comprising Sn, Al, Ga, In, Zr, Sb, Bi, Mg, Nb, Ta and Ti and which is in direct contact with the second barrier layer.
30. 11. A glazing panel in accordance with any preceding claim, in which the glazing panel is a heat treatable glazing panel.
35. 12. A glazing panel in accordance with any one of claims 1 to 10, in which the glazing panel is a substantially haze free heat treated glazing panel.

13. A glazing panel comprising a glass substrate onto which a coating stack has been deposited, in which the coating stack consists essentially of the following sequential layers:

5 a base antireflective layer comprising a base antireflective lower layer and a base antireflective upper layer which is of a different composition to that of the base antireflective lower layer,

10 the base antireflective lower layer comprising a mixed oxide of Zn and Sn having a ratio Sn/Zn ranging from 0.5 to 2 by weight

10 the base antireflective upper layer comprising a mixed oxide of Zn and Sn having a ratio Sn/Zn ranging from 0.02 to 0.5 by weight

10 a first infra-red reflecting layer comprising metallic silver

10 a first barrier layer

15 a central antireflective layer comprising a central antireflective lower layer and a central antireflective upper layer which is of a different composition to that of the central antireflective lower layer being in direct contact with the first barrier layer and comprising a mixed oxide of Zn and Sn having a ratio Sn/Zn ranging from 0.5 to 2

15 the central antireflective upper layer comprising a mixed oxide of Zn and Sn having a ratio Sn/Zn ranging from 0.02 to 0.5 by weight

20 a second infra-red reflecting layer comprising metallic silver

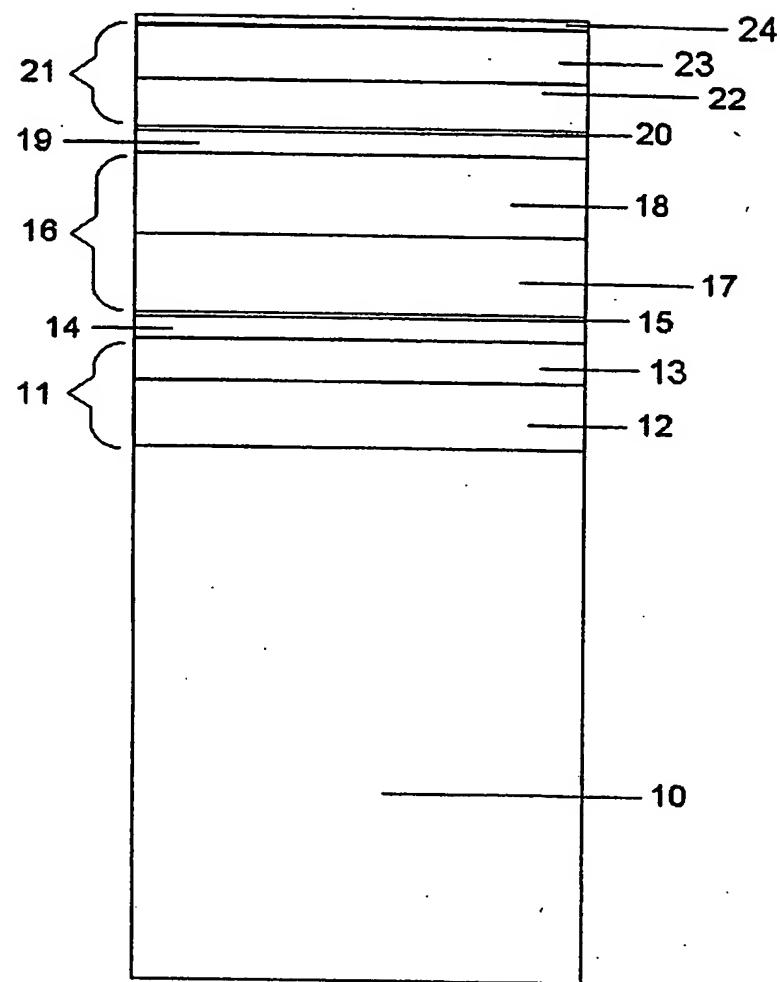
20 a second barrier layer

20 a top antireflective layer.

25 14. Use of a glazing panel in accordance with claim 13 in the manufacture a laminated glazing panel in which the glazing panel in accordance with claim 13 is heated and bent into its desired shape subsequent to deposition of the coating stack.

30 15. A method of manufacturing a glazing panel having a haze of less than about 0.5 comprising the step of subjecting a glazing panel in accordance with any one of claims 1 to 13 to a tempering and/or bending operation at at least 570 °C.

1/1

Fig 1

INTERNATIONAL SEARCH REPORT

In International Application No
PCT/EP 00/10278

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C17/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 747 330 A (LEYBOLD AG) 11 December 1996 (1996-12-11) abstract page 3, line 32 – line 45 claims 1-5,11	1-12, 15
A		13,14
P,X	WO 00 37381 A (GLAVERBEL ;DECROUPET DANIEL (BE); AOMINE NOBUTAKA (JP); EBISAWA JU) 29 June 2000 (2000-06-29) abstract examples 1,3 claims	1-5, 9-12,15

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *'A' document defining the general state of the art which is not considered to be of particular relevance
- *'E' earlier document but published on or after the International filing date
- *'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *'O' document referring to an oral disclosure, use, exhibition or other means
- *'P' document published prior to the International filing date but later than the priority date claimed

- *'T' later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&' document member of the same patent family

Date of the actual completion of the International search

15 January 2001

Date of mailing of the International search report

23/01/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Grenette, S

INTERNATIONAL SEARCH REPORT

Int'l Application No.
PCT/EP 00/10278

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 719 876 A (PPG INDUSTRIES INC) 3 July 1996 (1996-07-03) abstract column 3, line 21 - line 33 example 1 claims 1,5-7	1-15
P,A	WO 00 37380 A (GLAVERBEL) 29 June 2000 (2000-06-29) abstract example 1 claims	1-15
A	GB 2 229 737 A (GLAVERBEL) 3 October 1990 (1990-10-03) abstract examples	1-15
A	US 5 834 103 A (BOND ROBERT ET AL) 10 November 1998 (1998-11-10) abstract table 2 claims	1-15
A	US 5 279 722 A (ZMELTY ANTON ET AL) 18 January 1994 (1994-01-18) abstract column 2, line 32 - line 54 column 7; table claims	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/10278

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0747330	A	11-12-1996	DE 19520843 A DE 59601582 D ES 2132805 T JP 8336928 A KR 171175 B US 5962115 A	12-12-1996 12-05-1999 16-08-1999 24-12-1996 15-01-1999 05-10-1999
WO 0037381	A	29-06-2000	NONE	
EP 0719876	A	03-07-1996	AU 676974 B AU 3442795 A CA 2161283 A CN 1133899 A JP 8225943 A KR 179463 B US 6010602 A	27-03-1997 11-07-1996 28-06-1996 23-10-1996 03-09-1996 20-03-1999 04-01-2000
WO 0037380	A	29-06-2000	NONE	
GB 2229737	A	03-10-1990	BE 1002992 A CH 679580 A DE 3941027 A DK 635589 A FR 2641271 A JP 2289449 A JP 2876325 B LU 87646 A NL 8903147 A NO 174500 B SE 469523 B SE 8904231 A US 5110662 A	15-10-1991 13-03-1992 12-07-1990 06-07-1990 06-07-1990 29-11-1990 31-03-1999 10-07-1990 01-08-1990 07-02-1994 19-07-1993 06-07-1990 05-05-1992
US 5834103	A	10-11-1998	AT 169288 T CA 2189430 A DE 69503896 D DE 69503896 T DK 758306 T EP 0758306 A ES 2122595 T JP 10503745 T WO 9529883 A	15-08-1998 09-11-1995 10-09-1998 10-12-1998 10-05-1999 19-02-1997 16-12-1998 07-04-1998 09-11-1995
US 5279722	A	18-01-1994	DE 4135701 A DE 59204255 D EP 0543077 A ES 2079718 T JP 5221692 A	13-05-1993 14-12-1995 26-05-1993 16-01-1996 31-08-1993

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

FARMER, Guy

GLAVERBEL

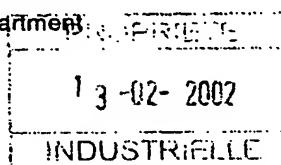
Intellectual Property Department

Center R. & D.

Rue de l'Aurora, 2

B-6040 Jumet

BELGIQUE



PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year) 11.02.2002

Applicant's or agent's file reference
4236 IRISHIP

IMPORTANT NOTIFICATION

International application No.
PCT/EP00/10278

International filing date (day/month/year)
13/10/2000

Priority date (day/month/year)
14/10/1999

Applicant
GLAVERBEL et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

WO-PCT; PROSEC

IPER

4752
SF

Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Koutsoftas, P Tel.+49 89 2399-7273
---	---



PATENT COOPERATION TREATY
PCT
INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 4236 IRISHIP	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP00/10278	International filing date (day/month/year) 13/10/2000	Priority date (day/month/year) 14/10/1999
International Patent Classification (IPC) or national classification and IPC C03C17/36		
<p>Applicant GLAVERBEL et al.</p> <p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p> <p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application 		

Date of submission of the demand 19/03/2001	Date of completion of this report 11.02.2002
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Fortunati, T Telephone No. +49 89 2399 8561



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP00/102

I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):
Description, pages:

1-10 as originally filed

Claims, No.:

1-15 as originally filed

Drawings, sheets:

1/1 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure of the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/EP00/102

the drawings, sheets:

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c));

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1
	No: Claims
Inventive step (IS)	Yes: Claims 1
	No: Claims
Industrial applicability (IA)	Yes: Claims 1
	No: Claims

2. Citations and explanations
see separate sheet

VIII Certain observations on the international application

See separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/10278

1) Reference is made to the following documents:

D1: EP-A-0 747 330 (LEYBOLD AG) 11 December 1996 (1996-12-11)
D2: WO 00 37381 A (GLAVERBEL ;DECROUPET DANIEL (BE); AQMINE
NOBUTAKA (JP); EBISAWA JU) 29 June 2000 (2000-06-29)

2) Regarding section VIII:

2.1) Claim 14 seems to be more a process-claim than a use-claim since it is defined by means of process-steps and not by means of use-features. Therefore, it would have been better to reformulate use-claim 14 as a process-claim according to the following formulation:
" Process of manufacturing a glazing panel according to claim 13 in which this glazing panel is heated and bent into its desired shape subsequent to deposition of the coating stack ".

2.2) Even if use-claim 14 had been reformulated as a process-claim according to the suggestion contained in point 2.1 above, claim 14 would have been nothing less than a repetition of present process-claim 15. Therefore, use-claim 14 should have been deleted. Present process-claim 15 should have been renumbered as process-claim 14.

2.3) Regarding the term " haze " in claim 15:
There should be a unit after the figure " 0.5 ". Moreover, the type of measurement of the " haze " should be defined. A definition of "haze" is not given in the description of the present application.

2.4) An independent product-claim should contain all the essential features to characterise the claimed product. It is not clear why the essential features of the glazing panel have been split into two different product-claims (independent product-claim 1 and independent product-claim 13). A single independent product-claim referring to a glazing panel and containing all the essential features of this glazing panel should have been filed. Non-essential features should have been confined in the sub-claims. Moreover, the fact that the essential features of the glazing panel are split into two different product-claims does not enable one to understand what is the scope of protection of the product-claims.

2.5) The scope of protection of product-claim 13 already seems to be contained in product-claim 1. Therefore, product-claim 13 merely appears to be a useless repetition of product-claim 1. Product-claim 13 should have been deleted.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/10278

3) Regarding section VIII:

3.1) "A" is not an SI unit. Use should have been made of SI units throughout the entire application.

4) Regarding section V:

4.1) Documents D1 and D2 already disclose a glazing panel comprising the substrate/layers indicated in claims 1 and 13 of the application (see the passages of D1 and D2 cited in the Search Report). Therefore, claims 1 and 13 are not considered as novel with respect to D1 and D2.

4.2) The dependent claims 2 to 12 are not inventive for the following reasons:

The dependent claims contain conventional information which in combination with the independent claims 1 would not result in a patentable subject-matter.

Docket No.: 4004-036-30

Declaration, Power of Attorney and Petition

WE (I) the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

GLAZING

the specification of which

- is attached hereto.
- was amended on 12 APRIL 2002
- was filed as PCT international application

Number PCT/EP00/10278

on 13 OCTOBER 2000

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
99203357.1	EP	14 OCTOBER 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)

And we (I) hereby appoint Steven B. Kelber, Reg. No. 30,073; Jerold I. Schneider, Reg. No. 24,765; Paul C. Kimball, Reg. No. 34,641; Wilburn L. Chesser, Reg. No. 41,668; James M. Heintz, Reg. No. 41,828; Amy L. Miller, Reg. No. 43,804; Lisa K. Norton, Reg. No. 44,977; Patrick R. Delaney, Reg. No. 45,338; and Christopher W. Raimund, Reg. No. 47,258, as our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to Supervisor, Patent Prosecution Services, Piper Rudnick LLP, 1200 Nineteenth Street, N.W., Washington, D.C. 20036-2412.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Jean-Michel DEPAUW
NAME OF SOLE INVENTOR

Residence: Jumet, Belgium

JEAN -MICHEL DEPAUW

Citizen of: BELGIUM

Signature of Inventor

Post Office Address: Rue de l'Aurore, 2

24 APRIL 2002

B-6040 Jumet

Date

BELGIUM